

COATING, MODIFICATION AND ETCHING OF SUBSTRATE SURFACE
WITH PARTICLE BEAM IRRADIATION OF THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to a surface treatment
5 technology including coating, modification and etching of a
surface of a substrate (such as a semiconductor wafer), in
particular, to a surface treatment technology using various
kinds of beams such as particle beams for facilitating
reaction of the surface to a source material used in the
10 surface treatment.

With the rapid achievement of finer and even more
densely packed semiconductor devices, the interconnect (or
circuit wiring) pitch has become markedly narrow, and the
interconnect electric density has increased considerably.
15 As a result, conventional semiconductor devices comprising
an interlayer insulative film layer of silicon oxide
and an aluminum-based conductor are confronted with
serious problems, i.e. an RC delay phenomenon in signal
transmission (i.e. a delay relating to electric resistance
20 and static capacitance) and electro-migration damage to the
conductor material. To solve such a problem, it has
recently been considered to be essential for the conductor
material to be changed from the presently used aluminum-
based material to copper, which has a lower electric
25 resistivity. Further, a coating technology referred to as
"chemical vapor deposition (CVD)" has been considered to be
most suitable for fabricating such copper interconnects
(for example, see NIKKEI MICRODEVICE, December 1998, p.32).

Fig. 1 is a schematic diagram illustrating an
30 exemplary configuration of a coating apparatus used for
copper-coating by the CVD technology. In Fig. 1, reference
numeral 1 designates a reaction chamber which has a
susceptor 2 arranged therein for loading a substrate Wf
thereon and is connected to a vacuum evacuation system such
35 as a vacuum pump or the like so as to be decompressed to a
specified value P. Reference numeral 3 designates a source
material container for containing a source liquid, from
which the source liquid is sent to a vaporizer 5 (at a flow

rate f) by supplying a carrier gas from a carrier gas container 4 to the source material container 3, so as to be vaporized therein and supplied into the reaction chamber 1 as a source gas 6. Further, the susceptor 2 is equipped 5 with a heater 7 therein for heating the semiconductor substrate Wf.

In the coating apparatus with a configuration described above, after an inner pressure of the reaction chamber 1 having been reduced to a predetermined pressure 10 P, the source gas 6 is introduced thereinto from the vaporizer 5 so as for copper included in the source gas to be dissociated and deposited onto a surface of the substrate Wf. As for the source material, an organic complex containing Cu as an component (e.g. 15 hexafluoroacetylacetunate-Cu(I)-trimethylvinyl-silane, liquid under ordinary temperature) is mainly used to be vaporized in the vaporizer 5, and the substrate Wf is heated up to 140 to 180°C to cause the reaction so that the copper may be deposited on the surface of the substrate Wf 20 having the recesses such as fine via holes and trenches formed thereon for forming the interconnect in the semiconductor device.

Figs. 2(a) and 2(b) are schematic cross sectional views of the recess respectively illustrating typical 25 conditions of deposition of copper: 1) coating; and 2) filling thereof. Fig. 2(a) shows a case of coating, in which a diffusion barrier 13 is formed on a surface of a fine recess 12 formed on an insulating layer 11 of a substrate, and a deposited copper layer 14 is formed on the 30 diffusion barrier 13 as the seed layer. Fig. 2(b) shows a case of filling, in which the coating as shown in Fig. 2(a) further proceeds and, as a result, the recess of the surface is finally filled with copper to form a copper layer 15 formed over the surface with the recess.

35 As described above, various problems are likely to occur when the fine recesses on the surface of the substrate are actually coated or filled with copper by CVD technology. That is, coating or filling the fine recess

with a width equal to or narrower than 0.13 μm with metal copper by ordinary CVD causes such problems that 1), as shown in Fig. 3(a), the surface of the formed coating film has considerable roughness (bad morphology), and 2), as 5 shown in Fig. 3(b), a defect such as void or seam is also likely to be produced in the copper filled in the recess due to a premature flow-choking forming in an inlet port or mouth of the recess prior to completely filling the inside thereof.

10 The reason why this phenomenon occurs is considered that a trend for a small number of nucleation sites to grow up into abnormally great size is dominant since an activity on a surface of the under-layer is inherently low and thereby a density of nucleation site of metal precipitation 15 is made to be extremely low.

As time passes, an island-like deposited copper layer 14 shown in Fig. 3(a) grows in a thickness and a volume so as for each of islands to coalesce with one another to eventually form a continuous film-like deposition, but 20 since the density of the nucleation site is low and the number of generated islands is small, as a result the deposited copper layer 14 formed after a certain period of time has a considerable rough surface, which presents the undesirable morphology.

25 A major reason why the void defect 16, as shown in Fig. 3(b), occurs in the recess 12 is considered that in the course of the filling process, the deposited copper layer 15 grows locally at an inlet port of the recess so as to be protruded from each side thereof to bridge the inlet 30 port and thereby the copper is prevented from flowing into the recess.

Since the Cu-CVD is typically performed under a pressure of several Torrs to several ten Torrs, a fluidity of gaseous phase is under a condition of viscous flow. 35 Accordingly, the source component reaches the surface of the substrate through a diffusion passing through a stagnant layer existing near by the substrate. Steep gradient in a source concentration generated in the

stagnant layer is thought to have a certain relation with the choking of the inlet port.

A deposition rate of copper by the CVD has been generally known to be fairly slow in comparison with that of sputter reflow, electro-plating or the like. Indeed, the former hardly exceeds the deposition rate of 200 nm/m, while the latter two easily accomplish approximately 500 nm/m.

Further, bonding strength between the copper deposition layer formed by the CVD and the substrate surface (surface of the diffusion barrier 13, for example, surface of TaN film) is small, there is a danger that electro-migration resistance might deteriorates as a result. The poor adhesive bonding property described above is considered to arise from the fact that a lattice incoherence exists between TaN and Cu, and that the surface of the TaN layer formed in the surface of the substrate by the conventional sputtering is then oxidized in a surrounding environment to be covered by the oxide film.

In connection with this, in order to solve the problem of the RC delay phenomenon in signal transmission and electromigration damage to the conductor material, there has been suggested a change of the material of the interlayer insulative film layer from the presently used silicon oxide to an organic material of low dielectric constant, in addition to the above-discussed proposal to change the material of the conductor material to copper. However, even if a diffusion barrier layer of a metal or a compound is deposited in contact with an interlayer insulative film layer of an organic material, a favorable adhesion (bond) strength cannot be obtained by a conventional practice because there is a large difference in properties between the materials of the two layers. Accordingly, the diffusion barrier layer is likely to peel or get loose by receiving a thermal or mechanical load after the deposition process. Thus, the conventional practice has a serious problem to be solved.

Organic materials usable in the near future to form

the interlayer insulative film layer include siloxane-based organic materials. A typical example thereof is MSQ (Methyl SilsesQuioxane), which is an organic SOD having a methyl group. Examples of pure materials containing no 5 siloxane are organic polymers (e.g. polyaryl ether and aromatic hydrocarbons). These organic materials have a dielectric constant of the order of 2.5 and are therefore considered to be most probable materials for next-generation interconnect structures (see, for example, the 10 August 1999 issue of Electronic Journal, p. 91).

Such an organic material and a metal or compound material commonly used to form a diffusion barrier layer in contact with the organic material are substantially different from each other in general properties, i.e. 15 physical, chemical, thermal and mechanical properties, to say nothing of molecular structure and interatomic (intermolecular) distance, in addition to the fact that the former is an organic material and the latter is an inorganic material. Therefore, it is difficult to make the 20 two materials adhere (bond) to each other. Even if the two materials can be made to adhere (bond) to each other, the adhesion strength (bond strength) is very small. Therefore, there is a strong possibility that the two materials will 25 peel or dissociate from each other upon receiving an in-process load during a semiconductor device manufacturing operation or an in-service load, causing an interruption of the manufacturing process or leading to stopping operation after the start of service.

According to the prior art, attempts have been 30 made to create an excellent bonded layer by physically roughening the surface of an insulating layer serving as an underlayer for a diffusion barrier layer before it is formed, or activating the surface of the insulating layer by a chemical treatment. However, the diffusion barrier 35 layer is originally a very thin film having a thickness of 10 to 50 nanometers. It is therefore difficult to obtain a suitable roughness for the thin diffusion barrier layer, and it is extremely difficult to form the inner surfaces of

fine recesses in the underlayer (insulating layer) into an optimum surface configuration. Further, the chemical activation treatment may cause pollution problems due to waste fluid. Therefore, it costs a great deal to treat the
5 waste fluid. Accordingly, the chemical activation treatment is not preferable from the practical point of view.

Meanwhile, it is conceivable to bring an active species (e.g. hydrogen radicals) into contact with the
10 surface of the interlayer insulative film layer to thereby reduce the surface of the underlayer or sever the atomic bond thereof in advance (pre-treatment). It is also conceivable to raise the temperature after the deposition of the diffusion barrier layer to thereby induce
15 interdiffusion or form a compound by a reaction between the two layers (post-treatment). However, because of an extremely large difference in physical properties between the materials of the two films, neither the pre-treatment nor the post-treatment produces significant effects. These
20 treatments may produce a contrary result, i.e. formation of a harmful reaction product.

Further, with regard to use of a copper as a conductive material in fabrication of a semiconductor device, there is another problem as discussed below.

25 To date, it has been considered to be quite difficult that an anisotropic etching (hereinafter referred to as an etching, where appropriate) is applied to Cu by way of dry etching method using a gas without any liquid agent applied thereto, and actually there has been found no such
30 successful example put into practical use. Among small number of research papers, there has been reported a result of a case where a reactive ion etching (RIE) was conducted by using a mixed gas composed of SiCl₄, Cl₂, N₂, and NH₃ [Arita et al. P.1156 in the Applied Physics, 61, 11 (1992)].
35 According to this paper, it is reported that a successful processing shape was obtained with an etching rate of about 100 nm/min as shown in Fig. 4. Herein, NH₃ gas was added to the material gas for the purpose of forming a protective

film of SiN family over the side wall face in order to maintain the directional property of the etching.

Nevertheless, there has been a problem in that the etching rate decreases as the flow rate of the NH₃ increases, as

5 shown in Fig. 4.

On the other hand, differently from the etching of the substrate of semiconductor, there has been disclosed a technology to be used for removing a copper film deposited in the interior of an apparatus for the chemical vapor

10 deposition (CVD) of copper, in which the copper film is brought into contact with gaseous hexafluoro-acetylacetone [C₅H₂O₂F₆, hereinafter abbreviated as H(hfac)] and oxygen gas so as to form a volatile copper complex compound [Tomoaki Koide et al. 30P-YA-16 in "The proceedings of the 47th

15 Applied Physics Related Association Lecture Meeting"

('00.3)]. The technology has taught that there occurs no reaction with the copper when the copper film is brought into contact with only the H(hfac) gas, but the H(hfac) gas added with O₂ gas causes such reactions as the oxidization 20 of the metal copper as denoted by the flowing formula (1) and the complexing and desorption of the copper oxide as denoted by the following formula (2), resulting in the deposited copper film to be vaporized and removed.

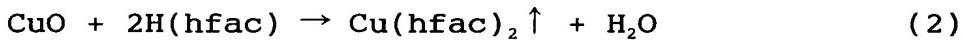
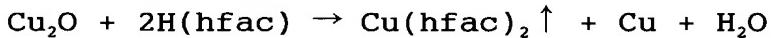
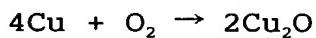


Fig. 5 is a diagram illustrating an example of actual measurement of removing rate of Cu reported in the above 30 paper. As can be seen from Fig. 6, the copper substrate heated up to 300°C is etched and removed with the rate of approximately 400 nm/min. However, if the principle disclosed in this paper is applied to the etching process in the semiconductor device fabrication without any 35 modifications, there would occur an isotropic etching as shown in Fig. 6, causing considerable disadvantages in wire-patterning of the semiconductor device.

Referring to Fig. 6, a Si substrate as designated by

17 has an insulation layer 14a, a Cu wiring layer 14, and a resist layer (mask) 18, each of which layers being sequentially built up one on another on top of the Si base layer 17, wherein if H(hfac) gas 19 is blown into an
5 aperture 18a of the resist layer 18 to etch the Cu wiring layer 14, resultant etch pit 12 formed by isotropic etching with the H(hfac) gas 19 expands in the lower location of the resist layer 18 to be greater than the cross sectional area of the aperture 18a, thus making it impossible for the
10 etch pit 12 to be formed limitedly in the vertically downward direction from the aperture 18a of the resist layer 18. That is, there have been problems associated with the prior art, including that the anisotropic (directional) etching of the Cu wiring layer is
15 impracticable.

SUMMARY OF THE INVENTION

The present invention is made in the light of the above-described circumstances.

An object of the present invention is to provide
20 method and apparatus applying a surface treatment to a surface of a substrate, the surface treatment being selected from a group consisting of the following surface treatments: coating, denaturation, modification and etching, the method comprising the steps of bringing a surface
25 treatment gas into contact with a surface of a substrate, and irradiating the surface of the substrate with a fast particle beam to enhance an activity of the surface and/or the surface treatment gas thereby facilitating the reaction between the surface and the gas.

In accordance with a first aspect of the present invention, there is provided a method of coating a surface of a substrate provided with fine recesses by a chemical vapor deposition technology, wherein the surface of the substrate is irradiated with a fast particle beam in such a manner that the beam reaches the surface of the recesses.
30 The irradiation is effected in parallel with and/or prior to, or alternatively with a supply of a source gas for the deposition.

A density of nucleation site of deposition on the surface of the substrate is greatly increased by the irradiation. As a result, a surface morphology of a deposition layer deposited on the surface of the substrate
5 is likely to be formed planer. In addition, the choking at the inlet port of the recess can be avoided and thereby the void defect can be prevented from occurring by adjusting the particle beam so that the irradiation intensity thereof may vary depending on the position on the surface of the
10 substrate so as to control or specify a dominating growth direction of the deposition layer. At the same time, the adhesiveness between the deposition layer and the surface of the substrate can be extremely improved since a mixing in an atomic level can be generated in an interface between
15 the deposition layer and the surface of the substrate by increasing irradiation energy.

The particle beam may be selected from the group consisting of an electron beam, an ion beam, an atomic beam or a molecular beam. The substrate may be a silicon
20 substrate for fabricating a semiconductor device and the recess formed on the surface of the substrate is a patterned recess for forming an interconnect of the semiconductor device. The source gas is an organic complex gas containing copper as an component thereof. It is
25 preferable to control the particle energy of the beam to be between 200 eV and 10 keV.

The present invention also provides an apparatus for conducting the above-stated method, in which the apparatus comprises at least an ion source necessary for generating a
30 particle beam, an ion accelerating mechanism, and a supply mechanism of a source gas containing an element for coating a surface of a substrate and the apparatus is equipped with a function for irradiating the substrate surface with the particle beam.

In accordance with another aspect of the present invention, there is provided an interconnect structure of a semiconductor device in which a strong bond is formed
35 between an interlayer insulative film layer consisting

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essentially of an organic material of low dielectric constant and a diffusion barrier layer formed from a thin film of a metal or a compound so that peel or dissociation will not occur at the interface between the two layers.

5 interconnect structure may include a conductive portion provided in contact with the diffusion barrier layer.

According to the present invention, a mixing area is formed in the vicinity of the interface between the interlayer insulative film layer and the diffusion barrier layer by
10 fast particle irradiation. In the mixing area, atoms or molecules constituting the interlayer insulative film layer and the diffusion barrier layer are mixed together.

The interconnect structure may be provided in a semiconductor device, in which the interlayer insulative film layer, the diffusion barrier layer and the conductive portion are formed in fine patterns. Preferably, the interlayer insulative film layer is made of a material selected from the group consisting of siloxane-based organic compounds and other organic polymers, and the
20 conductive portion is made of copper.

The present invention also provides a method of producing an interconnect structure by forming a diffusion barrier layer in contact with an interlayer insulative film layer, and forming a conductive portion in contact with the
25 diffusion barrier layer. The step of forming the diffusion barrier layer in contact with the interlayer insulative film layer includes a film deposition step of depositing a specified element and a particle beam irradiation step of performing irradiation with a particle beam. The film
30 deposition step and the particle beam irradiation step are carried out simultaneously or individually or alternately. Preferably, the particle beam irradiation step is carried out with a particle energy in the range of from 800 eV to 2 MeV.

It is generally known that during a thin film deposition process or after the deposition of a thin film, the thin film and the underlayer are irradiated with a fast particle beam, such as an ion beam, an atom beam or a

molecular beam, to induce mixing of atoms constituting the thin film and the underlayer in the vicinity of the interface therebetween. In the mixing area, a disorderly mixed state of atoms is usually obtained, in which the
5 regular crystal lattice arrangement is disordered remarkably. As the distance from such an disorderly mixed area increases, the arrangement of atoms gradually shifts to a regular arrangement similar to that before the fast particle irradiation.

10 It is known that when a boundary area between two layers is formed with a structure in which atoms constituting the two layers are mixed together as stated above, the area provides an extremely high adhesion strength (bond strength). According to the present
15 invention, a mixing area in which atoms constituting the interlayer insulative film layer and the diffusion barrier layer are mixed together is formed in the vicinity of the interface between the two layers by fast particle irradiation. Therefore, the interlayer insulative film
20 layer and the diffusion barrier layer are bonded together with a sufficiently high adhesion strength. Accordingly, it is possible to provide an interconnect structure free from the likelihood of peel or dissociation at the interface between the interlayer insulative film layer and
25 the diffusion barrier layer.

Fig. 7 shows the adhesion strength when polyethylene, which is substantially difficult to bond to any mating material by nature, is made to adhere to silicon (Si) by a deposition method using an ion beam [i.e. vacuum
30 evaporation and deposition of polyethylene on a Si substrate by a cluster ion beam method; excerpted from Kou Yamada "Thin Film Design by Ion Beam" (September 1991, Kyoritsu Shuppan), p. 108]. Despite a combination of two materials that are normally almost or one hundred percent
35 impossible to bond together, an adhesion strength as high as 5 to 15 kgf/cm² is obtained by appropriately selecting an ion accelerating voltage and an ion current. Thus, noteworthy characteristics are exhibited. This phenomenon

is considered attributable to mixing of atoms in the vicinity of the interface between the two materials induced by the ion irradiation. The phenomenon cannot rationally be explained otherwise.

5 In general, when a substrate is irradiated with a fast particle beam, e.g. a fast ion beam, atom beam or molecular beam, the effect of the beam irradiation on the substrate surface differs according to the particle energy.

Fig. 8 shows the tendency of penetration depth of
10 collided particles into a substrate when it is irradiated with a fast particle beam, together with principal actions applied to the substrate. As the particle energy increases, the penetration depth of particles into the substrate increases, and the principal actions shift from vacuum
15 evaporation and deposition onto the surface of the substrate through sputtering in the surface layer to implantation into the substrate and mixing. It is known that the mixing action occurs actively particularly when the irradiation particle energy is in the range of from
20 3 keV to 3 MeV as shown in Fig. 8, and atoms of the substrate that collide with the implanted particles are sputtered from the lattice and collide with neighboring substrate atoms successively. That is, cascade collision occurs, and thus lattice defects are produced. Mixing of
25 atoms caused by such cascade collision is the essence of the mixing action. The mixing action takes place most vigorously when the irradiation energy is in the above-described range of from 3 keV to 3 MeV.

When the mixing action occurs at a moderate depth,
30 the bond strength between the substrate and the deposited film on the substrate surface becomes remarkably high. This phenomenon is considered due to the fact that atoms or molecules constituting the deposited film and the substrate are mixed together by the mixing action. In the process
35 shown in Fig. 1, two materials that can hardly adhere to each other by nature are made to adhere (bond) together successfully by making good use of the mixing action. Thus, it is possible to perform film deposition with favorable

adhesion (bond) strength even for a combination of materials that have heretofore been regarded as impossible to bond to each other by using a fast particle beam with properly controlled energy.

5 Accordingly, the use of the fast particle beam action allows deposition of a diffusion barrier layer of a compound such as TaN, WN, TiN, TaSiN, WSiN or TiSiN or a metal such as Ta on an interlayer insulative film layer of an organic material with a sufficiently high adhesion
10 (bond) strength.

In accordance with a further aspect of the present invention, there is provided a method for performing an anisotropic etching of a substrate in a dry etching process, comprising the steps of: bringing a surface of a substrate 15 into contact with a fluid well reactive with a material of the substrate; compounding a gas including a component element of a material of the substrate resulting from a chemical reaction between the surface of the substrate and the fluid; and consequently removing the material from the 20 surface of the substrate sequentially, wherein a gas is used for the fluid well reactive with the material of the substrate, and further an activity is enhanced locally in a desired region in the surface of the substrate by irradiating the desired region with a beam selected from 25 the group consisting of an ultra violet beam, a laser beam, an electron beam, an atomic beam, a molecular beam, thus to allow an anisotropic etching to proceed.

This method will enable copper to be subjected to an anisotropic etching in dry etching process, while it has 30 been conventionally considered to be infeasible to subject copper to such an anisotropic etching. It is preferable that the particle energy of the beam is controlled to be between 200 eV and 1keV so that the particle beam brings about sputtering of atoms in the surface of the substrate 35 to enhance the activity of the irradiated region.

The present invention further provide an apparatus for performing an anisotropic etching of a substrate in a manner of dry etching, the apparatus comprising: a reaction

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chamber; an ion generating and accelerating mechanism used as a source for generating a particle beam, such as an ion beam or an atomic beam; and a reactive fluid supply mechanism for supplying a reactive fluid having a
5 reactivity with a material of the substrate, wherein the reactive fluid is supplied from the reactive fluid supply mechanism to the surface of the substrate disposed in a predetermined location within the reaction chamber, while the particle beam, such as the ion beam or the atomic beam,
10 is directed from the ion generating and accelerating mechanism against the surface of the substrate, so as to enhance an activity locally in a desired region in the surface of the substrate, and thus to allow the anisotropic etching to proceed.

15 Furthermore, the present invention provides an apparatus for generating a fast particle beam suitable for use in the method and apparatus in accordance with the present invention as stated above. The apparatus comprises a housing for receiving a predetermined gas, anode and
20 cathode plates provided in the housing with a predetermined spacing being interposed therebetween and arranged in parallel with each other, anode and cathode plates each being provided with a plurality of through holes, the spacing being set to be in the range of $D/14 - D$, in which
25 D is a diameter of the anode and cathode plates. The anode and cathode plates being adapted to be applied with a high voltage to cause a plasma discharge therebetween to ionize the gas thereby forming a fast particle beam. It is preferable to make the range of the diameter of the
30 electrode plates being in the rage of 1 mm - 14 mm.

The above and other objects, features and advantages of the present invention will become more apparent from the following description of the preferred embodiments thereof, taken in conjunction with the accompanying drawings.

35 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram illustrating an exemplary configuration of a coating apparatus according to a conventional CVD technology;

Fig. 2(a) is a schematic cross sectional view illustrating a coating condition of a substrate surface with a recess, which has been coated with copper;

5 Fig. 2(b) is a schematic cross sectional view illustrating a coating condition of the same substrate surface in which the coating has proceeded to an extent that the coating material fills the recess;

10 Fig. 3(a) is a schematic cross sectional view similar to Fig. 2(a), while illustrating a typical problem caused in a copper coating process in accordance with the conventional CVD technology;

15 Fig. 3(b) is a schematic cross sectional view similar to Fig. 2(b), while illustrating another typical problem, i.e., creating of a void;

Fig. 4 is a diagram illustrating an effect on a reactive ion etching rate for Cu caused by adding NH₃ to a mixed etching gas composed of SiCl₄, Cl₂, and N₂;

Fig. 5 is a diagram illustrating an example of actual measurement of a removing rate of Cu by H(hfac)+O₂ gas;

20 Fig. 6 is a schematic drawing for explaining an isotropic etching by H(hfac)+O₂ gas;

Fig. 7 is a diagram showing a relationship between the adhesion (bond) strength of polyethylene to a Si substrate and the ion accelerating voltage.

25 Fig. 8 is a diagram showing a relationship between penetration depth of particles into a substrate when it is irradiated with a fast particle beam and the particle energy of the fast particle beam, in which principal surface phenomena are noted.

30 Fig. 9 is a schematic drawing showing an exemplary configuration of a coating apparatus in accordance with the present invention.

Fig. 10(a) is a schematic cross sectional view illustrating a copper-coating process in accordance with the present invention for a surface of a substrate formed with a recess in which the surface is irradiated with a slanting hydrogen beam impinging onto the surface;

Fig. 10(b) is a schematic cross sectional view

illustrating the copper-coating process in which the hydrogen beam impinges onto the surface in a direction normal to the same;

Fig. 11 is a diagram similar to that of Fig. 8;

5 Fig. 12 is a schematic diagram showing a structural example of a deposition apparatus by evaporation and irradiation for producing an interconnect structure according to the present invention;

10 Fig. 13 is a schematic diagram showing a structural example of a cluster particle beam deposition apparatus for producing an interconnect structure according to the present invention;

15 Fig. 14(a) is a diagram showing an example of a duty operation for source gas supply in the interconnect structure producing method according to the present invention;

Fig. 14(b) is a schematic cross sectional view showing conditions of film deposition and mixing;

20 Fig. 15(a) is a diagram showing an example of a duty operation for source gas supply in the interconnect structure producing method according to the present invention;

25 Fig. 15(b) is a schematic cross sectional view showing a condition of film deposition and mixing;

Fig. 16(a) is a diagram showing an example of a duty operation for source gas supply in the interconnect structure producing method according to the present invention;

30 Fig. 16(b) is a schematic cross sectional view showing a condition of film deposition and mixing;

Fig. 16(c) is a schematic cross sectional view showing another condition of film deposition and mixing;

35 Fig. 17(a) is a diagram showing an example of a duty operation for source gas supply in the interconnect structure producing method according to the present invention;

Fig. 17(b) is a schematic cross sectional view showing a condition of film deposition and mixing;

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Fig. 17(c) is a schematic cross sectional view showing the conditions of film deposition and mixing;

Fig. 18 is a diagram showing a structural example of a fast particle beam irradiation apparatus for producing an 5 interconnect structure according to the present invention.

Fig. 19(a) is a schematic cross sectional view showing an interface between an organic insulating layer and a material filled in a recess formed in the insulating layer;

10 Fig. 19(b) is a schematic cross sectional view showing a model of interface peel that may occur during a chemical/mechanical polishing (CMP) process for polishing a deposited film.

15 Fig. 20 is a chart showing a flow of a process of producing an interconnect structure according to the present invention.

20 Fig. 21(a) is a schematic cross sectional view showing a mechanism of formation of a coating layer in a recess formed in a substrate according to a conventional vacuum deposition method;

Fig. 21(b) is a schematic cross sectional view showing a mechanism of formation of a coating layer in a recess formed in a substrate according to the conventional 25 vacuum deposition method;

Fig. 21(c) is a schematic cross sectional view showing a coating layer formed in a recess according to the conventional vacuum deposition method;

30 Fig. 21(d) is a schematic cross sectional view showing a coating layer formed in according to the conventional vacuum deposition method in which a void is formed in the portion of the layer filled in the recess;

35 Fig. 21(e) is a schematic cross sectional view showing a mechanism of formation of a coating layer over a surface provided with a recess by using a collimated beam of particles of a coating material in a conventional vacuum deposition method;

Fig. 21(f) is a schematic cross sectional view showing a coating layer formed over the surface by using

the collimated particle beam;

Fig. 22 is a schematic cross sectional view showing a coating method in accordance with the present invention;

Fig. 23(a) is a schematic cross sectional view
5 showing a defect formed in a coating layer which might be caused in a coating method according to the present invention;

Fig. 23(b) is a schematic drawing showing a way to avoid the defect in the coating layer as shown in Fig.
10 23(b);

Fig. 23(c) is a cross sectional view showing a coating layer formed on a surface having a recess according to the present invention;

Fig. 24 is a schematic cross sectional view showing a
15 "reflow" which may be caused in a process of forming a coating layer formed on the side wall of the recess;

Fig. 25(a)-25(d) are cross sectional views showing a method of coating a surface of a substrate in sequential order according to the present invention;

20 Fig. 26 is a schematic drawing illustrating a relationship between an inclination of a surface of a substrate relative to a source material beam supply direction and an amount of coating material particle beam entering a recess formed in the surface of the substrate;

Fig. 27(a) is a schematic cross sectional view showing a condition of a coating layer formed in accordance with the present invention;

Fig. 27(b) is a schematic cross sectional view showing a condition of the coating layer which has been
30 further developed as compared with that shown in Fig.
27(b);

Fig. 28 is a schematic cross sectional view of a semiconductor substrate fabricated in accordance with the present invention;;

35 Fig. 29(a)-29(d) are cross sectional views showing a method of coating a surface of a substrate in sequential order according to the present invention;

Fig. 30 is a cross sectional view of a semiconductor

substrate which has bee subjected to anisotropic etching according to the present invention;

Fig. 31 is a table showing exemplary combinations of etching gases and particle beams;

5 Fig. 32 is a schematic cross sectional view showing a mechanism of anisotropic etching in accordance with the present invention;

Fig. 33 is a diagram similar to that of Fig. 11;

10 Fig. 34 is a schematic drawing showing an exemplary configuration of a coating apparatus in accordance with the present invention.

Fig. 35 is a schematic drawing showing another exemplary configuration of a coating apparatus in accordance with the present invention.

15 Fig. 36(a) is a schematic cross sectional view showing an undesirable phenomenon which is likely to occur in an anisotropic etching in accordance with the present invention when using an ion beam;

20 Fig. 36(b) is a schematic cross sectional view showing a condition that anisotropic etching in accordance with the present invention has been preferably done by using a neutral particle beam;

25 Fig. 37 is a perspective view of a fast particle beam generating apparatus, a portion of the apparatus being taken away for the purpose of clarity;

Fig. 38 is a diagram showing a relationship between a product of gas pressure and distance between electrode plates and a voltage necessary for initiation of plasma discharge;

30 Fig. 39 is a diagram showing a relationship between a plasma density and an electron density in a plasma;

Fig. 40 is a schematic drawing showing an exemplary configuration of a coating apparatus in accordance with the present invention.

35 DETAILED DESCRIPTION OF THE INVENTION

Preferred embodiments of the present invention will now be described in detail with reference to the attached drawings.

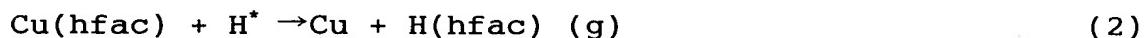
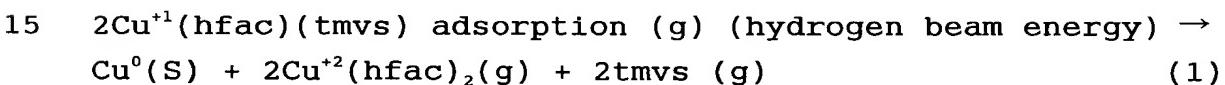
Fig. 9 is a schematic diagram illustrating an exemplary configuration of a coating apparatus by CVD technology according to the present invention. In Fig. 9, reference numeral 21 designates a reaction chamber which 5 has a susceptor 22 arranged therein for loading/holding a substrate Wf thereon, and an exhaust port 32 of the reaction chamber 21 is connected to a vacuum evacuation system equipped with a vacuum pump or the like so as to be decompressed to a specified pressure. Reference numeral 23 10 designates a source container for containing a liquid source, from which the liquid source is sent to a vaporizer 26 by supplying H₂ gas from an H₂ reservoir 24 via a flow controller 25 to the source container 23, so as to be vaporized in the vaporizer 26 and then to be supplied into 15 the reaction chamber 21 as a source gas 27.

Reference numeral 28 designates a fast ion generating mechanism for generating and applying an hydrogen (including hydrogen ion H⁺, hydrogen radical H^{*}, hydrogen molecular H₂, etc.) beam 29 onto the substrate Wf 20 loaded/held on the susceptor 22 in the reaction chamber 21, and the fast ion generating mechanism 28 is designed so as to be supplied with H₂ gas from the H₂ reservoir 24 via the flow controller 30. Reference numeral 31 designates a 25 heating/cooling mechanism integrated into the susceptor 22 for heating/cooling the substrate Wf. The present coating apparatus is designed such that the source gas is supplied from the external vaporizer 26 into the reaction chamber 21 so as to interact with the hydrogen beam to cause a 30 reaction such as decomposition/synthesis of the source material and eventually to deposit a desired amount of copper on the substrate Wf. In the source container 23, hexafluoroacetylacetunate-Cu(I)-trimethylvinyl-silane (hfac)(tmvs) is contained.

Figs. 10(a) and 10(b) show a process where a copper- 35 coating is applied to the fine recess (trench, hole, etc.) formed in the surface of the substrate Wf by the coating apparatus of Fig. 9. Fig. 10(a) shows a case where a surface of the recess is coated by a copper film, which is

mainly employed for forming a seed layer indispensable to the subsequent copper electro-plating. Fig. 10(b) shows another case where the coating is conducted to such an extent that the recess is filled with copper, whereby
5 electro-plating is not needed.

In either cases shown in Figs. 10(a) and 10(b), first the surface of the substrate absorbs the source material Cu (hfac)(tmvs) 33, then the fast hydrogen (including H^+ , H^* , H_2 , etc.) beam 29 is irradiated thereto to apply necessary
10 energy to the absorbed Cu (hfac)(tmvs) and eventually to decompose the source material to form the deposition of metal copper. The chemical reaction during the above processes is supposed to be represented by the reaction formulas (1), (2) below:



where, H^* is a hydrogen radical.

According to this embodiment, since the hydrogen beam
20 29 having high energy is directed to the surface of the substrate Wf, bindings between atoms on the surface of the diffusion barrier (TaN) 13 are released in innumerable points on the surface of the substrate. Since a surface energy is enhanced in a portion where the binding atoms is
25 broken, and as such portions emerges everywhere to promote the nucleation, the number of the nucleation sites is greatly increased.

On the other hand, since a surface diffusion rate of copper atoms generated by the decomposition of the source
30 material remains at the same level with that of an ordinary case where no irradiation by hydrogen beam 29 is effected, the granular deposition shown in Fig. 3(a) decreases in the size resulting in an increase in its numeral density. This enhances a planarization of the deposition layer allowing
35 to avoid a film deposition with fairly rough surface. In addition, as shown in Fig. 10(a), when the thin film is to be formed on the surface in the recess, a uniform and continuous thin copper film can be formed on a bottom and a

side walls by depositing copper while controlling the tilting angle of the irradiating direction of the hydrogen beam to make a density of nucleation uniform.

Further, when the irradiation direction of the 5 hydrogen beam 29 is restricted to be vertical to the bottom and to be parallel with the side walls of the recess formed on the surface of the substrate Wf as shown in Fig. 10(b), an irradiation energy density to the bottom is made to be extremely greater comparing with that on the side walls, 10 and consequently the decomposition or dissociation of the absorbed source molecular occurs substantially only on the bottom surface. Accordingly, the growth direction of the copper deposition is limited to one direction from the bottom toward the inlet port of the recess. As a result, 15 the choking at the inlet port of the recess caused by a protrusion (overhanging) of the deposited copper can be avoided, and thereby also the void defect 16 shown in Fig. 3(b) can be prevented from occurring.

According to the method of the present invention, 20 since the film deposition is performed under a normal operating pressure range of about 1×10^{-4} Torrs or lower, which is extremely lower than that of ordinary CVD, the film deposition can be performed in a so-called molecular flow area where a mean free path of the gaseous molecular 25 is greater than a size of the apparatus. Since there is no gas stagnant layer near by the surface of the substrate Wf because of the molecular flow space, which is different from a particle flow space for the conventional CVD, the deposition can be performed independent from a macroscopic 30 gas flow rate. In other words, relatively high speed deposition can be accomplished with smaller source gas flow rate allowing an improvement in source consumption efficiency. Further, in contrast with the fact that in the ordinary heat CVD the hydrogen dissociation hardly occurs 35 and accordingly only the reaction represented by the formula (1) occurs (which means that only a half of Cu contained in the source material is used), according to the method of the present invention since there exists abundant

active hydrogen such as hydrogen ion H^+ , hydrogen radical H^\bullet , and accordingly the reaction represented by the formula (2) also is likely to occur, the Cu otherwise possibly wasted as the components of the exhaust gas in the ordinary CVD
5 can be used effectively to be precipitated and deposited. As can be understood also from this point, the deposition rate is increased (theoretically twice as fast as the current one) and also the source utilization factor can be improved.

10 Further, since by irradiating the hydrogen beam 29 of 200 eV to 10 keV, there occurs not only the sputtering on the surface of the substrate Wf but also an atomic level mixing in the interface between the copper deposition layer and the substrate caused by an inward penetration of the
15 hydrogen (see Fig. 6), the adhesive/bonding property between the copper deposition layer and the substrate is greatly improved. Although the hydrogen beam is employed as the particle beam in the above embodiment, it is a matter of course that another type of beam may be used.

20 A useful effect may be brought about by irradiating a substrate with the hydrogen beam prior to the supply of the copper source gas. This is due to fact that the nucleation site in the under-layer is increased by releasing/reducing a part of the atomic bindings in the
25 surface of the TaN layer, which serves as the diffusion barrier of the under-layer, and/or allowing the hydrogen to be adsorbed/penetrated onto the surface thereof.

Although in the above embodiment copper (Cu) is deposited on the surface of the substrate, the material to
30 be deposited is not limited to copper, and another metal may be employed therefor.

In accordance with the above-stated embodiment, since a density of nucleation site of deposition on the surface of the substrate is greatly increased by irradiating a
35 particle beam onto the substrate either in conjunction with or prior to the supply of the source gas, a surface morphology of the deposition layer deposited on the surface of the substrate is likely to be planer. In addition,

choking at the inlet port of the recess can be avoided and thereby the void defect can be prevented from occurring by adjusting the particle beam so that the irradiation intensity thereof may vary depending on the position on the 5 surface of the substrate, so as to control or specify a dominating growth direction of the deposition layer, and at the same time, the adhesiveness between the deposition layer and the surface of the substrate can be greatly improved by causing mixing at an atomic level in the 10 interface between the deposition layer and the surface of the substrate by the irradiation of the particle beam.

Further, since the coating apparatus of the embodiment comprises the ion source, the ion accelerating mechanism and the source supply mechanism, and is adapted 15 to irradiate the particle beam onto the substrate in parallel with the process for applying the ordinary chemical vapor deposition and/or prior to the supply of the source gas, therefore a surface morphology of a deposition layer deposited on the surface of the substrate is likely 20 to become planar, and by controlling the dominating growth direction of the deposition layer, choking at the inlet port of the recess can be avoided and thereby a void defect can be prevented from occurring, and at the same time the adhesiveness between the deposition layer and the substrate 25 can be greatly improved.

With reference to Figs. 12-20, another type of embodiments of the present invention will be explained.

Fig. 12 is a diagram showing a structural example of a deposition apparatus by evaporation and irradiation for 30 producing an interconnect structure according to an embodiment of the present invention. In Fig. 12, a deposition chamber 201 contains a crucible 203 accommodating a Ta source 202. A heater 204 is provided around the outer periphery of the crucible 203. By heating 35 the crucible 203 with the heater 204, Ta vapor 301 is emitted in the deposition chamber 201.

In addition, an ion source 205 and a neutralizer 206 are placed in the deposition chamber 201. When the ion

source 205 is supplied with N₂ gas 302, N ions are generated from the ion source 205. The N ions are passed through the neutralizer 206 to form a N particle (atom) beam 303. The N particle beam 303 is directed to irradiate 5 a substrate 208, e.g. a semiconductor wafer, held on a substrate holder 207. That is, in the deposition apparatus, irradiation with the N particle beam 303 is performed in parallel to the vacuum evaporation and deposition of Ta. The aim of this arrangement is to synthesize TaN and to 10 cause mixing of evaporated substances in the substrate 208.

It should be noted that the deposition chamber 201 is provided with an inlet port 209 for a source gas and a shutter 210 for blocking the passage of the Ta vapor 301 and the N particle beam 303 to stop the irradiation of the substrate 208. Further, the deposition chamber 201 is provided with an evacuation port 211 connected to a vacuum evacuation system (not shown) to evacuate the deposition chamber 201.

In the deposition apparatus shown in Fig. 12, the
vacuum evaporation and deposition of the Ta vapor 301 and
the irradiation with the N₂ particle beam 303 may be
performed simultaneously or individually or alternately.
It is conceivable to use various duty operations
appropriately according to need. In the process shown in
Fig. 12, N₂ is supplied in the form of the N₂ gas 302.
However, it is also possible according to circumstances to
use TaN as a source material and to supply Ar to the ion
source 205, thereby irradiating the substrate 208 with a
fast Ar particle beam. It is also possible to introduce a
source gas containing Ta from the inlet port 209 instead of
using a source material, for example.

Fig. 13 is a diagram showing a structural example of a cluster particle beam deposition apparatus for producing an interconnect structure according to another embodiment 35 of the present invention. In Fig. 13, the same reference numerals as those in Fig. 12 denote the same or equivalent portions. A TaN source 212 is placed in the crucible 303. The source 212 is heated by irradiation with electrons from

an electron gun 213 to generate N₂ gas and Ta vapor in the form of a N particle beam 303 and a Ta particle beam 204. These particle beams 303 and 204 are directed to irradiate the substrate 208. The deposition chamber 201 further 5 contains an electron accelerating electrode 214, an electron emission source 215, an accelerating electrode 216, a neutralizer 217 and a heater 218. In this process, TaN is used as a source material, and this is applied to the substrate 208 in the form of Ta and N cluster particle 10 beams.

Figs. 14 to 17 are diagrams showing examples of the duty operation for source gas supply performed by using the deposition apparatuses shown in Figs. 12 and 13, together with the conditions of film deposition and mixing. 15 Regarding the source supply mode in the deposition apparatus shown in Fig. 12, the Ta vapor 301 and the N particle beam 303 are supplied simultaneously and continuously in many cases. In general, however, it is also possible to supply a part of the source materials in 20 other modes. Thus, various supply methods as shown in Figs. 14 to 17 can be executed.

Fig. 14 is a diagram showing a process in which film deposition and mixing are effected by supplying a Ta particle beam and a N particle beam simultaneously and 25 continuously. As shown in Fig. 14(a), the Ta particle beam 204 and the N particle beam 303 are simultaneously and continuously supplied in specified fixed quantities, respectively, to irradiate the substrate 208. Consequently, as shown in of Fig. 14(b), a TaN film layer 233 is 30 deposited over the surface of an organic insulating film layer 230 formed on the surface of the substrate 208 (not shown). At the same time, a mixing layer 231 is formed in the vicinity of the interface between the TaN film layer 233 and the organic insulating film layer 230. In the 35 mixing layer 231, atoms constituting the organic insulating film layer 230 and the TaN film layer 233 are mixed together.

Fig. 15 is a diagram showing a process in which film

deposition and mixing are effected by continuously supplying Ta vapor and intermittently supplying a N particle beam. As shown in of Fig. 15(a), the Ta vapor 301 is continuously supplied in a specified fixed quantity, and 5 the N particle beam 303 is intermittently supplied in a specified fixed quantity. Consequently, as shown in of Fig. 15(b), a TaN film layer 233 is deposited over the surface of an organic insulating film layer 230 formed on the surface of the substrate 208 (not shown). At the same 10 time, a mixing layer 231 is formed in the vicinity of the interface between the TaN film layer 233 and the organic insulating film layer 230. In the mixing layer 231, atoms constituting the organic insulating film layer 230 and the TaN film layer 233 are mixed together.

15 Fig. 16 is a diagram showing a process in which film deposition and mixing are effected by supplying Ta vapor and a N particle beam alternately. As shown of Fig. 16(a), the Ta vapor 301 and the N particle beam 303 are alternately supplied in specified fixed quantities, 20 respectively. Consequently, as shown in Fig. 16(b) and 16(c), a TaN film layer 233 is deposited over the surface of an organic insulating film layer 230 formed on the surface of the substrate 208 (not shown), and in parallel to the formation of the TaN film layer 233, a mixing layer 25 231 is formed in the vicinity of the interface between the TaN film layer 233 and the organic insulating film layer 230. In the mixing layer 231, atoms constituting the organic insulating film layer 230 and the TaN film layer 233 are mixed together.

30 Fig. 17 is a diagram showing a process in which film deposition and mixing are effected by supplying a N particle beam after the supply of Ta vapor. As shown in Fig. 17(a), the Ta vapor 301 is supplied in a specified fixed quantity, and thereafter, the substrate 208 (not 35 shown) is irradiated with the N particle beam 303 in a specified fixed quantity. Consequently, as shown in Fig. 17(b), a Ta film layer 232 is deposited on the surface of an organic insulating film layer 230 formed on the

surface of the substrate 208 (not shown). Thereafter, the Ta film layer 232 is converted into a TaN film layer 233, and at the same time, a mixing layer 231 is formed in the vicinity of the interface between the TaN film layer 233
5 and the organic insulating film layer 230. In the mixing layer 231, atoms constituting the organic insulating film layer 230 and the TaN film layer 233 are mixed together.

In the deposition apparatuses shown in Figs. 12 and 13,
10 the generated ions themselves may be used as particles to irradiate the substrate 208. Alternatively, the charged particles may be converted into neutral particles by operating the neutralizer 206 (217) before being applied to the substrate 208. In the process of manufacturing semiconductor devices, if there is likelihood of the
15 devices being damaged by being charged excessively, it is desirable to use a neutral atom or molecular beam obtained by the operation of the neutralizer 206 (217) as irradiation particles instead of charged particles such as ions.

20 Regarding the processes shown in Figs. 14 to 17, the process in which film deposition and mixing are effected simultaneously is known as "dynamic mixing". The process in which mixing is caused after the completion of film deposition is known as "static mixing".

25 Fig. 18 is a diagram showing a structural example of a fast particle beam irradiation apparatus for applying the above-described fast particle beam, which is different in configuration from those shown in Figs. 12 and 13. The fast particle beam irradiation apparatus has a processing chamber 241. The processing chamber 241 is provided with a gas inlet port 246 and an evacuation port 247. The evacuation port 247 is connected to a vacuum evacuation system (not shown) to evacuate the processing chamber 241. In the processing chamber 241, a turntable 242 for mounting
30 a substrate 243 is rotatably installed. A fast particle beam source 245 is provided in the upper part of the processing chamber 241. The fast particle beam source 245 has a center axis a specified angle (θ) tilted from the

vertical direction with respect to the surface of the substrate 243. By introducing Ar gas 205 into the fast particle beam source 245, a fast Ar atom beam 206 is produced to irradiate the substrate 243, which has a film 5 244 formed on the surface thereof.

As the fast particle beam source 245, a publicly known parallel-plate DC plasma type fast particle beam source (see, for example, the specification and drawings of Japanese Patent Application No. Hei 7-86542) is used. The 10 overall length of this fast particle beam source 245 in the direction of the gas stream is made much shorter than normal (narrow gap type; see, for example, Kai Tokuyama "Semiconductor Dry Etching Techniques" (October 1992, Sangyo Tosho) pp. 241-243, and the specification and 15 drawings of Japanese Patent Application No. 2000-254790), thereby realizing a uniform distribution of plasma, a high plasma density and a reduction in overall size. In this system, further, the fast Ar atom beam 206 is blown into a molecular flow area in the processing chamber 241 from a 20 large number of small hole-shaped nozzles. Therefore, argon atoms fly parallel to each other in the processing chamber 241 and collide with the substrate 243.

As shown in Fig. 18, the turntable 242 with the substrate 243 mounted thereon rotates during processing. 25 Therefore, even if the substrate 243 has minute recesses in the surface thereof, Ar atoms in the fast Ar atom beam 206 reach various portions inside the recesses, including the side walls, depths and bottoms of the recesses. Thus, the whole diffusion barrier layer adheres and bonds strongly to 30 the interlayer insulative film as the underlayer.

Naturally, the fast particle beam irradiation apparatus shown in Fig. 18 is usable under operating conditions other than the above (for example, under conditions where different gas species and deposition layer materials are 35 used and/or a neutralizing mechanism is required). For example, only Ta is deposited on the surface of the substrate 243 in advance, and N₂ gas is supplied in place of Ar, thereby allowing synthesis of TaN and simultaneously

inducing a mixing action by the fast nitrogen atom beam. Further, if a source gas is introduced from the gas inlet port 246 shown in Fig. 18, the fast particle beam irradiation apparatus can perform the same function (film deposition and mixing) as that of the deposition apparatuses shown in Figs. 12 and 13.

To estimate the necessary value for the adhesion (bond) strength of the deposited film, let us imagine a simple model by assuming, as shown in part (a) of Fig. 19, a gap fill element 253 as an interconnect portion of a semiconductor device. The gap fill element 253 comprises a two-dimensional diffusion barrier layer 251 of width b and height d , which has a unit thickness, and a conductive path 252. Let us assume that the gap fill element 253 peels uniformly at a side wall surface as shown in part (b) of Fig. 19 during a chemical/mechanical polishing process by receiving transverse polishing frictional force F from a rotary polishing table (not shown). In Fig. 19, reference symbol P denotes a mean contact surface pressure acting on the rotary polishing table. Reference numeral 254 denotes an organic insulating film layer formed on the surface of a substrate (not shown). Reference numeral 255 denotes a peel portion of the diffusion barrier layer 251 peeled from the organic insulating film layer 254.

In Fig. 19, when the mean contact surface pressure P acts on the rotary polishing table, the polishing frictional force F acts on the gap fill element 253 with a unit thickness so as to move the element 253 transversely. The polishing frictional force F is given by the following equation (1):

$$F = \mu Pb \quad (1)$$

where μ represents a mean friction coefficient.

Assuming that resistance force [=adhesion (bond) strength] acting per unit area when a side surface of the diffusion barrier layer 251 is uniformly separated by the polishing frictional force F is σ and the contribution of adhesion at the bottom surface is ignored, the following equation (2) holds:

$$F = \sigma d \quad (2)$$

From Eqs. (1) and (2), σ is expressed in the form of the following equation (3):

$$\sigma = \mu Pb/d \quad (3)$$

- 5 For safety, let μ be 0.3, and the mean contact surface pressure P is assumed to be $P=10$ kgf/cm² as a maximum estimated value in the actual machine. The aspect ratio is assumed to be $d/b=1/4$ as a minimum estimated value. On this assumption, $\sigma=13.5$ kgf/cm² is obtained from Eq. (3).
- 10 In other words, the adhesion strength between the organic insulating film layer 254 and the diffusion barrier layer 251 needs to be at least 13.5 kgf/cm². In the process of peeling, strictly speaking, separation along interface starts from a local region (weakest portion) of the joint area between the two layers 254 and 251. The peel load is smaller than force required for the interface between the organic insulating film layer 254 and the diffusion barrier layer 251 to separate all at once in the vertical direction as in the model shown in Fig. 19. Here, it is supposed for 15 explanatory simplicity that all the regions of the interface separate simultaneously, as stated above.
- 20

In conclusion, it will be understood with reference to Fig. 7 that the accelerating voltage needs to be at least 800 V (at least 800 eV in terms of particle energy) 25 in order to obtain the necessary adhesion (bond) strength by making use of mixing. On the other hand, it is convenient to set a particle energy upper limit at 2 MeV with a view to lessening the damage to semiconductor devices, although the maximum energy at which a mixing 30 action takes place is of the order of 3 MeV, as will be clear from Fig. 8. It will be understood from the foregoing discussion that the range of desirable particle energy values is from 800 eV to 2 MeV.

Fig. 20 is a chart showing the flow of a process for 35 producing an interconnect structure according to the present invention. At step ST1, an organic insulating layer of an organic polymer is formed on the surface of a substrate by coating or the like. Subsequently, holes and

trenches are formed on the surface of the organic insulating layer by lithography and etching at step ST2. Next, at step ST3, a diffusion barrier layer of TaN or the like is formed by particle beam irradiation with the deposition apparatus shown in Fig. 12. At the same time, the bond between the barrier layer and the organic insulating layer is strengthened (i.e. an area is formed in the vicinity of the interface between the organic insulating layer and the diffusion barrier layer, in which atoms constituting the two layers are mixed together).

Next, at step ST4, a seed layer is formed by sputtering, CVD or the film deposition method according to the present invention. Subsequently, interconnect filling is carried out by plating at step ST5 (i.e. interconnect paths constituting interconnect portions are formed in the holes and trenches covered at the surfaces thereof with the seed layer). Alternatively, after the diffusion barrier layer has been formed at the above-described step ST3, interconnect filling is carried out directly by reflow sputtering, CVD or the film deposition method according to the present invention. Whether to proceed from step ST3 to steps ST4 and ST5 or to step ST6 should be decided according to the degree of fineness of the interconnect structure or according to the need in the actual practice. Upon completion of the above-described interconnect filling, global planarization is carried out by chemical/mechanical polishing (CMP) at step ST7.

Although the deposition apparatus shown in Fig. 12 is used in the formation of the diffusion barrier layer at the above-described step ST3 by way of example, it is also possible to use various methods such as those described in connection with Figs. 13 to 18. The process consisting of the above-described steps ST1 to ST7 is repeated according to the number of interconnect layers.

As has been stated above, in accordance with the embodiments explained with reference to Figs. 12-20, following advantageous effects will be attainable.

As stated above, a mixing area is formed in the

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vicinity of the interface between the interlayer insulative film layer and the diffusion barrier layer by fast particle irradiation. In the mixing area, atoms or molecules constituting the interlayer insulative film layer and the diffusion barrier layer are mixed together. Therefore, the interlayer insulative film layer and the diffusion barrier layer are bonded together with a sufficiently high adhesion (bond) strength. Accordingly, it is possible to provide an interconnect structure free from peel or dissociation at the interface between the interlayer insulative film layer and the diffusion barrier layer.

Further, the interlayer insulative film layer is made of a material selected from the group consisting of siloxane-based organic compounds and other organic polymers, and the conductive portion is made of copper. Therefore, it is possible to provide an interconnect structure in which peel or dissociation will not occur at the interface between the interlayer insulative film layer and the diffusion barrier layer, and the RC delay phenomenon in signal transmission is minimized, and which is free from electromigration damage.

According to the interconnect structure producing method of the embodiment, the step of forming a diffusion barrier layer in contact with an interlayer insulative film layer includes a film deposition step of depositing a specified element and a particle beam irradiation step of performing irradiation with a particle beam. The film deposition step and the particle beam irradiation step are carried out simultaneously or individually or alternately.

Accordingly, a mixing area in which atoms or molecules constituting the interlayer insulative film layer and the diffusion barrier layer are mixed together is formed in the vicinity of the interface between the two layers. Consequently, the interlayer insulative film layer and the diffusion barrier layer are bonded together with a sufficiently high adhesion (bond) strength. Therefore, it is possible to provide an interconnect structure free from peel or dissociation at the interface between the

interlayer insulative film layer and the diffusion barrier layer.

Further, the particle beam irradiation step is carried out with a particle energy in the range of from 5 800 eV to 2 MeV. Therefore, a mixing area in which atoms or molecules constituting the interlayer insulative film layer and the diffusion barrier layer are mixed together is formed satisfactorily in the vicinity of the interface between the two layers. Moreover, there is no likelihood 10 that the particle energy may damage the device.

In connection with the embodiment shown in Fig. 18, another aspect of the present invention will be explained hereinbelow. That is, in the embodiment, a collimated particle beam 306 is used and the substrate 243 is rotated 15 while keeping an angle between the surface of the substrate 243 and the direction in which the beam 306 impinges upon the surface constant, whereby the interior of an interconnect (or circuit wiring) pattern recess formed in the surface is appropriately irradiated with the beam so 20 that the organic insulating film layer 230 is uniformly formed over the entire surface of the interconnect pattern recess formed in the surface of the substrate.

This aspect of the present invention is applicable to a vapor vacuum deposition method used for coating a surface 25 of a substrate. With reference to Figs. 21(a) - 21(d), there is shown a manner in which a surface of a substrate provided with an interconnect pattern recess 402 is coated by means of a conventional vacuum vapor deposition. As shown in Figs. 21(a) and 21(b), in a conventional vacuum 30 vapor deposition method, particles of a coating material are supplied in a non-collimated beam form, many particles impinge on the surface of the recess near the entrance opening of the recess and, thus, the number of the particles which reach the bottom portion of the recess 35 becomes small so that the coating layer formed on the surface of the recess grows rapidly at around the entrance opening of the recess as compared with that formed at around the bottom of the same (Fig. 21(c)). Accordingly,

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when the coating has proceeded to such an extent that the recess is filled with the coating material, a void might be formed in the coating material filled in the recess. In order to avoid such a formation of a void, there has been
5 made a proposal that coating particles are directed to the surface of the substrate as a collimated beam in a direction normal to the surface (Fig. 21(e)). However, in such a case, since few particles impinge on the side walls of the recess, the coating layer does not grow on the side
10 walls (Fig. 21(f)).

The present invention solve such a problem by employing a particle beam application method similar to that in the embodiment of Fig. 18. That is, as shown in Fig. 22, a coating material is supplied as a collimated
15 particle beam 413 and a substrate is inclined relative to the direction in which the beam is directed at a predetermined angle and is rotated about an axis parallel to the beam direction. In a full revolution of the substrate about the axis, the entire side surface of the
20 recess 414 is irradiated with the particle beam, whereby the problems stated with reference to Figs. 21(a) - 21(f) are solved. In order to enable the beam to reach the bottom surface of the recess, the inclination angle θ of the surface of the substrate relative to the beam direction
25 is set as follows:

$$0 < \theta < \theta_0 (= \tan^{-1}(A/2B))$$

wherein A is a mouth width of the recess and B is a depth of the same.

However, presuming that the beam is not perfectly
30 collimated, even if θ_0 is made larger, some amount of particle may reach the bottom surface of the recess.

If the coating is effected with the inclination angle θ of $\tan^{-1}(A/2B)$, there is a tendency that at the center of the bottom the coating layer becomes thick as compared with
35 that of the other portions. To avoid such a tendency, the inclination angle θ is set as being

$$\tan^{-1}(A/2B) < \theta < \tan^{-1}(A/B), \text{ and,}$$

if being set at around the above-noted upper limit, i.e.,

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tan⁻¹(A/B), the coating layer of a uniform thickness will be formed across the entire bottom surface of the recess (Fig. 23(c)). Further, taking into account the "re-sputtering" mentioned later, it is preferable to set the inclination angle of the surface of the substrate to fall into a range of 0° - tan⁻¹(A/B).

The above-noted discussion is based on an assumption that all the particles impinging the surface of the recess adhere to the surface at a position of impingement and there is no sputtering phenomenon in which particles which has once adhere to the surface is collided with another particle thereby being forced to be dissociated from the surface and displaced to another position on the surface. However, it is considered that the sputtering actually is, as shown in Fig. 24, likely to occur, although the degree of the sputtering differs depending on the various conditions including energy of collision between the particle, a kind of material forming the substrate, and a kind of the particle. In the case that such a sputtering occurs at a high level, many particles which were once deposited on the side wall are likely to be displaced towards the bottom of the recess and, thus, even if the inclination angle is set large so that the particle beam can not directly reach the bottom surface of the recess, the bottom surface will be coated with such displaced particles 413'. Sputtering may take place when energy of an impinging particle is more than a threshold of 30 - 50 eV (see "Sputtering Coating" by Haruhito Kobayashi published by Nikkan Kogyo Shinbunsha in April, 1998). While a rate of occurrence of sputtering increases as the energy of an impinging particle increases and becomes maximum when the energy of the impinging particle is around 30 keV, it decrease when the energy of the impinging particle exceeds the maximum value. From a such viewpoint, it is noted that the energy of an impinging particle should be set within a scope of 30 eV - 30 keV.

Fig. 25(a) - Fig. 25(d) and Figs. 29(a) - 29(d) show a progress of formation of a coating layer over a surface

of a substrate provided with a recess 414. It is preferable that the coating is conducted in a manner as stated below. In summary, at an initial stage, the bottom surface is mainly coated by setting the surface of the
5 substrate to be generally normal to the beam direction and then entire surface of the recess is coated by changing an angle of the surface of the substrate relative to the beam direction so that an aspect ratio (i.e., depth/mouth width of a recess: B_1/A_1 , B_2/A_2) is kept generally constant or
10 gradually decreases. As shown in Fig. 26, assuming that a rate of coating over a surface normal to a beam direction is "V", a rate of coating over a side wall of a recess 414 of a substrate 412 having an inclination angle θ becomes "V sin θ ". This means that rate of coating over the side wall
15 of the recess increases as the inclination angle θ increases. Thus, in a case that particles forming a coating layer over the side wall of the recess is subject to a so-called "reflow" or particle (or layer material) shift or towards the bottom of the recess by, for example,
20 sputtering as mentioned above, it is possible that the coating or filling of the recess is effected at a high rate by adjusting the inclination angle θ to be large without an danger of formation of a void in a coating layer filled in the recess 414 as mentioned with reference to Fig. 21(d).
25 Figs. 27(a) and 27(b) shows a progress of formation of coating in the recess 414 of the substrate 412 which proceeds accompanying the above-stated "reflow". The coating method can apply to formation of a copper interconnect (or circuit wiring) structure on a
30 semiconductor substrate 511 as shown in Fig. 28, the structure 27 comprising a barrier layer 515, a seed layer 517 and a copper interconnect layer 516.

In the above-stated coating method, the collimated beam is arranged taking into consideration the following
35 matters. For example, assuming that in a nitrogen atmosphere and the pressure is set to be 0.1 Pa, a nitrogen molecule can fly through a straight path of about 66 mm without collision with another nitrogen molecule. In other

words, a nitrogen molecule has a mean free path of about 66 mm. As the pressure of the atmosphere decreases, the mean free path expands. Specifically, when the pressure decreases to 0.01 Pa, the mean free path becomes 660 mm.

- 5 In the coating method of the present invention, the particle beam is arranged such that the particles reach the surface of the substrate through its mean free path without substantial collision thereof.

The present invention further provides method and
10 apparatus for conducting a dry etching, in particular, an anisotropic etching which is suitable for forming a fine pitch copper interconnect (or wiring) pattern in a semiconductor substrate.

Following is an explanation of the anisotropic
15 etching method in accordance with the present invention.

Fig. 30 is a conceptual drawing illustrating the anisotropic etching method. In this figure, reference numeral 611 designates a Si substrate, and an insulation layer (SiO_2) 612 and a Cu interconnect (or wiring) layer 20 613 are formed on a top of the Si substrate 611, and, further, a resist layer 614 provided with an interconnect or wiring pattern aperture 614a is formed on a top of the wiring layer 613.

The anisotropic etching is carried out by bringing a
25 mixture of H(hfac) gas and O_2 gas into contact with the substrate, while at the same time applying a radiation of Ar^+ ion or Ar radical beam 615 to the surface of the resist layer 614 on the substrate. The Cu interconnect layer 613 is etched through the aperture 614a of the resist layer 614
30 in a vertical direction.

In this etching process, when the H(hfac) gas and O_2 gas adsorbed on the surface or staying in the gas phase in the vicinity of the surface of the substrate (Cu interconnect layer 613) is exposed to the radiation of Ar^+ ions or Ar atoms, and further the pressure of gas phase and the energy of particles in the radiation beam is adjusted appropriately, an amount of deposition of component elements of the gas staying in the gas phase to the

TECHNICAL DRAWING

substrate surface can be increased, and at the same time a reactivity in the exposed region can be enhanced by the energy imparted to the gas and the Cu wiring layer 613 and the sputtering occurring in the exposed region of the
5 substrate surface. The relatively active reaction occurs in a region of the Cu wiring layer 613 having higher radiation beam density of Ar⁺ ions or Ar atoms (the bottom portion of the cavity 616), in comparison with in the side wall portion, which allows the anisotropic etching to
10 proceed.

Although the mixture composed of H(hfac)gas and O₂ gas is used for an etching gas in Fig. 30, the application is not limited to this but, for example, as shown in Fig. 31, the H(hfac) gas may be used solely as the etching gas in
15 combination with a radiation beam 615 of oxygen ions or oxygen radicals applied to the substrate.

Fig. 32 is a conceptual drawing illustrating an etching progress according to the combination shown in Fig. 31. When the beam 617 of oxygen ions or oxygen radicals is
20 irradiated and at the same time the H(hfac) gas is supplied as described above, then it turns out that the oxygen is intensively supplied to the region having higher radiation beam density on the surface where the H (hfac) molecules are absorbed, which consequently causes a reaction defined
25 as Cu → Cu₂O → Cu(hfac)₂, limitedly in the bottom portion of the cavity to make the anisotropic etching proceed on the Cu wiring layer 613. Fig. 32 is different from Fig. 30 in that the energy for reaction is given by the beam 617 of oxygen ions or oxygen radicals.

30 In this regard, the above reference [Tomoaki Koide et al. 30P-YA-16 in "The proceedings of the 47th Applied Physics Related Association Lecture Meeting" ('00.3)] has suggested that, as regards a procedure for bringing the substrate into contact with the gas in the case where the
35 H(hfac) gas and the oxygen are used for the etching gas, preferably the H (hfac) would be solely introduced at first and then the oxygen is added. This is considered to be due to the faster reaction, which could be accomplished when

the H(hfac) is allowed to be adsorbed on the surface of the Cu wiring layer 613 at first and then the oxygen is supplied later since the conversion of substance defined in the following equation (3) proceeds concurrently triggered
5 by the effect of excessive H(hfac) existing in the system.



Although it has been considered that the temperature (170°C) as high as that for Cu-CVD is appropriate for
10 inducing the reaction by, as a substitute for the form of the particle energy, only applying the heating, the above combination of the H(hfac) gas and the beam 617 of oxygen ions or oxygen radicals makes it possible for the fast etching to be carried out by the above-mentioned mechanism
15 while controlling the generation of residues by the yielded substances without using any heat-up mechanism. Further, since the reaction occurs significantly actively in the bottom portion of the cavity 616 in comparison with that in the side wall when also the oxygen beam is used, based on
20 the same principle as in the case of the Ar beam, therefore the anisotropy in etching can be accomplished.

As having been described, using the above method for etching the substrate makes it possible to perform the anisotropic dry etching of Cu, which otherwise would be
25 practically unfeasible in the prior art.

Preferably, the particle energy should be within a range of 200 eV to 1 keV. The reason for that is described below. Fig. 33 is a diagram illustrating a relation between a particle energy and a penetration depth of the
30 particle beam as well as those dominant phenomena occurring in the exposed surface of the substrate. When the sputter cleaning (i.e. physical etching) is applied to the surface of the substrate using a normal sputtering device, the Ar ions having energy of approximately 200 to 1,000 eV is
35 utilized as a sputtering gas (see Fig. 33). That is, it could be appreciated that the use of the Ar ions having the energy in the range causes the sputtering of the atoms in the surface of the substrate.

In this concern, the sputtering onto a copper surface using, for example, the Ar ions of 1,000 eV with the ion current density of 0.85 mA/cm² results in an measured etching rate of approximately 34 nm/min, which is extremely slow [P. 233 in "The practical Auger Electron Spectroscopy" edited by Ryuichi Shimizu and Kazuhiro Yoshihara, first edition in Jun., 1989 by Kyoritsu Publication Co., Ltd]. Accordingly, if the application is limited to the purpose of dry-cleaning of the surface (i.e. surface decontamination), the Ar ion etching may be useful, but it is extremely inefficient for the technology to be used for sharpening the surface into a desired shape and for creating a cavity. In brief, due to its extremely slow etching rate, there would be no possibility for the Ar ion etching to be applied in practice to a processing apparatus for mass production.

It should be noted, when the uniformity within the surface becomes problematic, which may be caused by an electro static charging on the substrate side or a dispersion of ions caused by mutual repulsion thereof when the ion beam radiation is applied, a radiation of neutral molecular or atomic beam might be used instead of the ion beam radiation.

The typical value for the physical etching rate obtained by using solely the Ar ions, which has conventionally been applied mainly to the researches, is approximately 30 nm/min as described in the above reference [P. 233 in "The practical Auger Electron Spectroscopy" edited by Ryuichi Shimizu and Kazuhiro Yoshihara, first edition in Jun., 1989 by Kyoritsu Publication Co., Ltd], and that is significantly slow in comparison with the rate of about 400 nm/min obtained easily by the reactive etching (RIE) performed in the semiconductor manufacturing process.

As described above, when the copper surface is etched by using the method for anisotropic etching of the substrate according to the present invention, the doubled etching effect is obtained by; 1) the etching caused by chemical action of the H(hfac) gas; and 2) the etching

caused by the physical action of the Ar ions, which take effect at the same time.

As discussed above, when the temperature of the substrate is set to 300°C, as shown in Fig. 5, the etching rate of about 400 nm/min is obtainable for 1) the etching by the chemical action, and further when the accelerating voltage for the Ar ions is set to 1,000 V, the etching rate of about 30 nm/min is obtainable for 2) the etching by the physical action. Accordingly, if both of 1) the etching by the chemical action and 2) the etching by the physical action concurrently take effect, it may be possible to easily achieve the etching rate equal to or more than ten times as high as the etching rate obtained by using the Ar ions only, thus providing a novel effect by way of the anisotropic (directional) etching means for patterning Cu wiring in the semiconductor device.

Further, the anisotropic etching according to the present invention, in comparison with the typical plasma etching method, has the following advantages. The method of the present invention is different from the typical dry etching (e.g. RIE) in that the former does not require the substrate to be placed in the plasmatic environment and the controlled etching process may be applicable. If the substrate is placed in the plasmas environment, there will be such problems to be possibly caused that the substrate and the surroundings will be contaminated by unnecessary by-products produced in the chemical reactions between the etching gas and the substrate and member material, and that the expected etching action could be disturbed by the etching gas starting decomposition before reaching to the substrate.

According to the present invention, a desired etching process can be performed under the condition where the above-mentioned undesired effects by the plasma are completely eliminated. Further, since the present invention prevents the temperature of the substrate surface from rising up excessively, which otherwise might possibly caused by applying plasma, another advantage may be

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provided in that the further aggregation and granulation of the deposited copper may be avoided. Owing to the advantages described above, the method for performing the anisotropic chemical etching of the substrate according to 5 the present invention makes it practical to apply the anisotropic dry etching to Cu, which has been conventionally considered infeasible, and thus greatly contributes to the fabrication of the semiconductor device having a Cu wiring structure.

10 It should be appreciated that, in the above embodiment, the description has been developed with respect to the example where the substrate of Cu is etched, but the substrate is not limited to Cu. That is, provided is an anisotropic dry etching method in which a substrate is 15 brought into contact with a fluid well reactive with the substrate to compound a gas containing an component element of the substrate by way of chemical reaction therebetween, thereby allowing the surface of the substrate to be sequentially removed, and accordingly, the substrate other 20 than Cu may be used so far as the activity can be locally enhanced to allow the anisotropic etching to be performed by using an organic gas for the fluid well reactive with the substrate and additionally applying to a desired region in the substrate surface at least one beam selected from 25 the group consisting of an ultraviolet beam or a laser beam, an electron beam or a charged particle beam, and an atomic beam or a molecular beam. Further, depending on the kind of the substrate, the inorganic gas other than the organic gas may be used.

30 Fig. 34 is an exemplary drawing illustrating a conceptual configuration of an anisotropic etching apparatus for performing the anisotropic etching method for a substrate according to the present invention. In Fig. 34, reference numeral 620 generally designates a reaction 35 chamber, and a substrate 622 is supported by a susceptor 621 and is mounted in an upper portion of the reaction chamber 620. The substrate 622 may be, for example, such a substrate as shown in Fig. 30, comprising the insulation

layer 612, the Cu wiring layer 613, and the resist layer 614 with the wiring processing pattern formed thereon, each layer being sequentially deposited one on the another on the surface of the Si substrate 611. In Fig. 34, the 5 substrate is mounted such that a resist layer 622a formed on the surface of the Cu wiring layer of the substrate 622 is directed downward. It is to be noted that a heating/cooling mechanism 621a for heating/cooling is arranged within the susceptor 621.

10 A fast ion generating mechanism 623 for generating an Ar⁺ ion beam or an Ar atom beam is disposed in the lower portion of the reaction chamber 620 so as to face to the resist layer 622a. The reaction chamber 620 is coupled to a vacuum evacuation system 624. Reference numeral 25 15 designates a H(hfac) container for storing H(hfac) gas, and the H(hfac) container 625 is connected with a He reservoir 628 for storing He gas via a mass flow controller (MFC) 626. The reaction chamber 620 is designed to be supplied with the H(hfac) gas by supplying He gas from the He reservoir 20 25 628 to the H(hfac) container 625 via the mass flow controller (MFC) 626. The reaction chamber is adapted to be further supplied with O₂ gas from an O₂ gas source 630 via a mass flow controller (MFC) 629. Further, the fast ion generating mechanism 623 is adapted to be supplied with 25 Ar gas from an Ar gas source 631.

In the anisotropic etching apparatus described above, when the H(hfac) gas and O₂ gas are supplied into the reaction chamber 620, and the radiation of the Ar⁺ ion beam or the Ar atom beam is directed toward the substrate 22 30 from the fast ion generating mechanism 623, an energy is transferred from the Ar⁺ ion or Ar atom to the H (hfac) gas and O₂ gas absorbed in the surface or staying in the gas phase in the proximity of the surface of the substrate 622, in similar way to that as shown in Fig. 30. Then, since 35 the relatively active reaction occurs in the bottom portion of the cavity of the Cu wiring layer having the higher radiation beam density of Ar⁺ ion of Ar atom, in comparison with in the side wall portion, therefore the anisotropic

etching is allowed to proceed.

Fig. 35 is an exemplary drawing illustrating another conceptual configuration of an anisotropic etching apparatus for performing the anisotropic etching method for 5 a substrate according to the present invention. In Fig. 35, similar parts are designated with the same reference numbers as in Fig. 34. The anisotropic etching apparatus in Fig. 35 is different from that in Fig. 34 in that the former comprises an ion neutralizing mechanism 632 for 10 electrically neutralizing the ions arranged in the upper portion of a fast ion generating mechanism 623. The fast ion generating mechanism 623 is designed so as to be supplied with O₂ gas from an O₂ gas source 633. The 15 anisotropic etching in the anisotropic etching apparatus with the above configuration occurs in the similar manner to that as described with reference to Fig. 32.

Employing the ion neutralizing mechanism 632 for electrically neutralizing ions as described above facilitates the apparatus to have a larger bore. That is, 20 in a case where the charged particle beam, such as an ion beam, is used, since respective particles have the homopolar electric charges, the particles tend to repulse against one another with the longer beam distance, which has often been true especially for the apparatus with the 25 larger bore. Consequently, the gradient of the etching direction is more likely to increase in the outer periphery of the substrate 622, as shown in Fig. 34 (a). In contrast, using the neutral particle beam generated by neutralizing the ions allows the irradiated rays to be maintained as 30 directed parallel as shown in Fig. 34 (b), thereby resolving the above problems and facilitating the fabrication of the apparatus with the larger bore. Further, since the irradiated particles are electrically neutral, any damages of the substrate 622 possibly caused by the 35 excessive charges are avoidable.

With reference to Fig. 37, there is shown a fast particle beam generating apparatus 701 in accordance with the present invention which is suitable for use in the

D E C I P T I O N
S U B S T R A T E
P A R T I C L E
G E N E R A T I O N
A P P A R A T U S

embodiments of the present invention described above. As shown, the fast particle beam generating apparatus 701 comprises a cylindrical vacuum housing 702 having an upper end closure 704 provided with a source gas intake fitting 703. The housing 702 is provided in its inside with disc-like electrode plates 705, 706 and 707 which are arranged in that order in parallel with the upper end closure 704 with the electrode plate 707 being positioned at the lower end of the housing 702. At least one of pairs of the neighboring electrode plates 705 and 706 and 706 and 707 has a spacing d in the range from 1 mm to 14 mm between the neighboring electrode plates. In other words, the spacing between the neighboring electrode plates is sized to be in the range of $D/14 - D$, wherein the "D" is a diameter of the electrode plate. Only for the sake of clarity, in Fig. 37, the spacing d is shown as being generally the same as the diameter D of the electrode plate.

In this embodiment, the electrode plates 705, 706 and 707 are connected to a common high direct current voltage source so that the electrode plates 705 and 707 become cathode plates and the electrode plate 706 positioned between the electrode plates 705 and 707 becomes an anode plate. The electrode plates 705, 706 and 707 are respectively provided with a plurality of holes 708 for allowing gas particles to pass therethrough. As shown, among the electrode plates, the electrode plate 705 has the least number of holes 708 and the electrode plates 706 and 707 have the same number of holes 708.

In the fast particle beam generating apparatus, particle beams are generated in a manner as stated below. A source gas is introduced into the vacuum housing 702 through the fitting 703 to fill the spaces between the electrode plates 705, 706 and 707. Then, electric discharge is caused between the neighboring electrode plates 705 and 706 and 706 and 707 to generate a plasma or a highly ionized gas. The ionized gas particles are then discharged outside the housing through the holes 708 of the electrode plate 707, while being subjected to electrical

neutralization when they pass through the holes 708 of the electrode plate 707, whereby a plurality of fast beam of electrically neutral particles are generated.

As stated above, in a conventional fast particle beam generating apparatus, it is common for the electrode plates to be separated at a long distance of about 140 mm. Thus, a great difference in the plasma density in the housing thereof is brought about in such a manner that the density becomes maximum at the center of the gap between the electrode plates and gradually decreases towards the electrode plates. Accordingly, it is impossible for the conventional fast particle beam generating apparatus to uniformly discharge particles during its operation. Such a characteristic is not suitable to be used in conducting a precise surface treatment of a semiconductor substrate including coating and etching as explained in connection with the embodiments described above.

In contrast, the fast particle beam generating apparatus in accordance with the present invention comprises at least one pair of parallel electrode plates for subjecting gas introduced therebetween to an electric discharge to generate a plasma, the distance between the electrode plates being small, i.e., in the range from $D/14$ to D , wherein "D" is a diameter of the electrode plate, specifically, in a range from 1 mm - 14 mm. Consequently, the plasma density difference as discussed above decreases to enable the particle beams to be uniformly discharged from the particle beam generating apparatus. It enables the apparatus to be preferably used in conducting a precise surface treatment of a semiconductor substrate.

The reason why the distance between the adjacent electrode plates should be set in the range from 1 mm to 14 mm will be explained below.

According to Paschen's Law, a direct current voltage V for triggering an electric discharge is decided by $P \times d$, in which "P" is a gas pressure and "d" is a distance between the adjacent electrode plates. Fig. 38 shows relationships between " $P \times d$ " and particular gases, i.e.,

sulfur dioxide, air, and hydrogen. In a conventional fast particle beam generating apparatus, the voltage "V" is set generally to 1 - 3 kVDC and "Pd" is set in the range about of 0.4 - 1.5 mm·Torr (about 53.2 - 186.2 mm·Pa) depending
5 on a kind of gas. Accordingly, assuming that a conventional operation conditions are V=1 kV, d=140 mm and P=1.33Pa, Pd becomes 186.2 mm·Pa and, thus, the electric discharge initiation characteristic is generally represented by a curve of the air in Fig. 38.

10 As shown in Fig. 38, in the case of "air", "Pd" corresponding to an electric discharge initiation voltage at 1kV is 186.2 mm·Pa, if "D" is 14mm in this embodiment, "P" becomes 13.3 (186.2/14) Pa which is ten times as much as the conventional gas pressure. As the gas pressure
15 increases, the plasma density increases accordingly thereby enabling a surface of a semiconductor substrate to be treated at a high speed. Namely, by decreasing the distance D between the adjacent electrode plates, the plasma is improved in its density and uniformity to thereby
20 make the fast particle beam generation apparatus to be appropriately used in conducting the surface treatment of a semiconductor substrate.

As discussed above, in order to treat a substrate at a high speed, it is necessary for the fast particle beam generating apparatus to have a high ion density, or to generate a high plasma density of, for example, 10^{11} -
25 $10^{12}/\text{cm}^3$. A plasma density generated by a conventional glow discharge is around $10^{10}/\text{cm}^3$ which is about 1 - 10% of the necessary density. Fig. 39 shows relationships between an electron density and a gas pressure during a plasma
30 discharge. As shown, as the gas pressure increases ten times from 1.33Pa to 13.3 Pa, the electron density increases about five times from $7 \times 10^{11}/\text{cm}^3$ - $3.3 \times 10^{12}/\text{cm}^3$. It is thus noted that as the gas pressure increases ten
35 times, the electron density increases about five time.

Assuming that the electron density and the plasma density correspond to each other, by increasing the gas pressure ten times from 1.33 Pa to 13.3 Pa, the plasma

density increases from $10^{10}/\text{cm}^3$, which is obtained in a conventional apparatus, to $10^{11} - 10^{12}/\text{cm}^3$. Namely, in order to set the distance between the adjacent electrode plates "D" to be 14 mm in the range of 1 mm - 14 mm, it is
5 necessary to increase the gas pressure 10 times thereby obtaining a high plasma density or high density and high speed ions.

It is advantageous that, when a plurality of gasses are used for surface treatment of a semiconductor substrate,
10 the Penning ionization is employed in which metastable excited particles collide with neutral particles to ionize the neutral particles. In order to causing one or more collision between metastable excited particles and neutral particles in a vacuum housing 702, it is necessary for the
15 distance "d" between the adjacent electrode plates must be larger than a mean free path of particles in the vacuum housing 702. That is, the following must be satisfied:

$$d > \lambda \quad (1)$$

Generally, the following relation stands between the
20 gas pressure P (Pa) and the free path λ :

$$\lambda \doteq 1.33/P \quad (2)$$

Assuming that the gas pressure P is 13.3 Pa, from (1)
and (2)

above, the following is led:

$$25 \quad d > 1.33/13.3 = 1 \times 10^{-1}\text{cm}$$

$$d > 1 \text{ mm}.$$

From the forgoing, it is decided that, by setting the distance between the adjacent electrode plates "d" to be in the range from 1 mm to 14 mm, a uniform plasma density can
30 be obtained so that the fast particle beam generating apparatus can be used in conducting a surface treatment of a semiconductor substrate in a uniform and high speed operation manner.

Although, at present, the diameter of most of
35 semiconductor wafers is 200 mm, it is expected that semiconductor wafers of 300 mm in diameter will be used for production of a part of semiconductor devices. The present invention can apply to treatment of such a large diameter

wafer. Namely, the present invention can apply to treatment of such a large size of semiconductor substrate by employing electrode plates of 300 mm in diameter, provided that maintaining the distance between the adjacent 5 electrode plates in the range of D/14 - D.

It should be noted that the present invention can apply to semiconductor substrate of any diameter sizes.

Further, it is preferable that the fast particle beams are subject to a so-called "choke effect" when they 10 pass holes 708 of the electrode plate 707 to exit the vacuum housing 702 so that the circumstances relating to the beams in the inside of the housing is independent from those of the outside of the housing. This enable the 15 inside of the housing 702 to be stable regardless of any changes in the circumstances outside the housing 702 which might be caused at a surface of a substrate to be treated. Further, the space downstream of the fast particle beam generating apparatus may be used as an intermediate flow or 20 molecular flow zone in which a substrate is placed to be subjected to anisotropic etching, modification, or coating.

With reference to Fig. 40, there is shown a surface treatment (or coating) apparatus which is substantially the same as the coating apparatus explained with reference to Fig. 9 except that the former apparatus employs the fast 25 particle beam generating apparatus as shown in Fig. 37 in place of the beam generating means denoted by reference numeral 28 in Fig. 9. The surface treatment apparatus includes a reactor housing 720 provided with the fast particle beam generating apparatus 701 at the bottom 30 thereof. At the top of the reactor housing, there is provided a substrate susceptor 722 having heating and cooling functions which holds a substrate 721 in such a manner that a surface thereof to be subjected to a treatment faces the fast particle beam generating apparatus 35 701. The reactor housing is further provided with a vacuum evacuation means (not shown) for generating a vacuum in the reactor housing.

Furthermore, the surface treatment apparatus includes

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a gas supply means comprising a hydrogen gas container 710. The hydrogen gas is introduced into the gas particle beam generating apparatus 702 through a flow regulator 711 and the gas intake fitting 703 of the fast particle beam generator.

The hydrogen gas is also supplied to a reservoir 713 of an organic complex source liquid or hexafluoroacetylacetunate-Cu(I)-trimethylvinylsilane. The source liquid is evaporated by an evaporator 714 and supplied to the reactor housing 720.

In the surface treatment apparatus, coating of copper is conducted as follows. The source liquid of hexafluoroacetylacetunate-Cu(I)-trimethylvinylsilane evaporated by the evaporator 714 is supplied into the reactor housing 720 which has been decompressed.

Simultaneously, hydrogen in the container 710 is supplied into the vacuum housing 702 of the fast particle beam generating apparatus 701. The hydrogen introduced into the vacuum housing is subject to a plasma discharge in such a manner as stated above. The ions generated by the plasma discharge fly into the reactor housing 702 through holes 708 of the electrode plate 707 of the fast particle beam generating apparatus while being subjected to electrical neutralization thereof when they pass through the holes 708 of the electrode plate 707, whereby neutral fast atom beams is formed. The beams irradiate the source material i.e., hexafluoroacetylacetunate-Cu(I)-trimethylvinylsilane adsorbed on the surface of the substrate 721 to facilitate deposition of the copper over the surface of the substrate 721.

It will be clear that the fast particle beam generating apparatus 701 is applicable to the various embodiments of the present invention described above to facilitate utilization of irradiation of a fast particle beam to a surface of a substrate to enhance various advantageous effects which are inherently brought about by with the embodiments.

It should be noted that the present invention is not

limited to the foregoing embodiments but can be modified in a variety of ways.

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